A Study of the Inhalation Exposure of Workers to Methyl Bromide and Chloropicrin During Preplant Soil Fumigations (Shallow Injection) in 1982 -- A Preliminary Report

by

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SUMMARY

The concentrations of methyl bromide and chloropicrin in the breathing zone of preplant soil fumigation workers were monitored in Orange County in September 1982. Monitoring was conducted during two fumigations. Adverse weather conditions and other work commitments prevented additional monitoring work. The monitoring results for methyl bromide showed levels well below the Cal/OSHA Permissible Exposure Limit (PEL) of 15 ppm. The highest level found was 6.3 ppm for one sampling period on the copilot. The chloropicrin results showed concentrations ranging from below the limit of detection (1.0 ppb) up to 181 ppb. Calculated time-weighted averages (TWA) for chloropicrin exposures were below the established PEL of 0.1 ppm.

INTRODUCTION

Methyl bromide and chloropicrin are Toxicity Category I pesticides. Mixtures of the two chemicals are registered for use in California as a preplant soil fumigant. The mixture is used to kill weed and grass seeds, nematodes, and other soil-borne organisms.

Methyl bromide is a colorless, tasteless, nonflammable gas which is odorless except at extremely high concentrations (2). With sufficient dosage, it is known to cause damage to the lungs, nervous system, kidneys and skin. The onset of symptoms from overexposure can be delayed for up to several hours. The PEL for methyl bromide is 15 ppm for an 8-hour TWA in the workplace environment. The Cal/OSHA ceiling (level not to be exceeded) for methyl bromide is 50 ppm.

Chloropicrin is a heavy nonflammable liquid. The odor threshold is reported from 0.78 ppm to 1.1 ppm (3,4). Concentrations of 0.3 ppm result in painful irritation to the eyes in approximately 3 to 30 seconds (1). No threshold level for eye irritation was found in the literature. The 8-hour PEL for chloropicrin is 0.1 ppm in the workplace environment. No Cal/OSHA exposure ceiling has been set for chloropicrin, but using the guidelines in Title 8, Section 5155 of the California Administrative Code, 0.3 ppm would be the recommended maximum exposure concentration. The American Conference of Governmental Industrial Hygienists have recommended a Threshold Limit Value (the TLV is the same as the PEL) of 0.1 ppm and a Short-Term Exposure Limit (STEL) of 0.3 ppm (1). These recommendations were made to provide freedom from eye irritation and prevent potential pulmonary changes.

APPLICATION

The major use period of the methyl bromide/chloropicrin mixture as a soil fumigant to fallow fields is from early July to early October. The methyl bromide and chloropicrin are premixed in compressed gas cylinders by the registrant. The mixture is shank-injected into the soil approximately eight inches deep using a positive pressure closed system (pressurized with nitrogen gas). A one mil polyethylene tarp is automatically laid down over the soil behind the shanks. The tarp reduces the dissipation rate of the gases into the air which lessens the hazards to the workers and increases the overall efficacy of the gases.

MATERIALS AND METHODS

Monitoring was conducted on workers performing three types of activities. They were the "driver," who operates the tractor; the "copilot," an individual seated at the rear of the tractor rig who takes care of routine problems with the application and/or equipment; and the "shoveler," who shovels soil on the perimeter of the tarp, sealing the fumigant under the tarp. The samples were collected in the breathing zone of each worker.

The sampling period for both methyl bromide and chloropicrin was approximately 45 minutes. Methyl bromide was trapped on charcoal sorbent tubes (SKC# 226-09, Lot 120), while the chloropicrin was trapped on two XAD-4 resin tubes

(SKC# 226-30-11-04, Lot 146) connected in series. Separate MSA model C-210 portable pumps were used with each type of tube. The counters on the C-210 portable pumps were calibrated to determine the ml/count ratio. The pumps were calibrated to pull approximately 200 ml of air/minute. The counters were read before and after each sample period. The net count was multiplied by the ml/count ratio to determine the volume of air (in ml)/sample.

All samples were capped and placed on dry ice and shipped to the Department's laboratory for analysis. In the laboratory, the sampling tubes were divided into sections to determine if breakthrough occurred, indicating nonquantitative trapping of methyl bromide or chloropicrin. The charcoal tubes were separated into front and back sections with each section analyzed separately. See Appendix 1 for the analytical method for methyl bromide. The chloropicrin sample was analyzed in three parts to check for migration through the tubes and to detect the amount of breakthrough, if any, into the third section. The first section was the whole first tube, the second was the front portion of the second tube, and the third was the back portion of the second tube. See Appendix 2 for the analytical method for chloropicrin.

RESULTS

The methyl bromide results were compared to the results from monitoring work done in 1981 (see HS-900). The 1982 results were found to be similar to the previous results (see Table 1 for the 1982 data). The levels found were well below the PEL of 15 ppm. Of the 11 samples taken, the highest level found was 6.3 ppm. Although statistical analysis was not done on the data (due to a limited number of samples), Graphs 1 and 2 show some correlation between the exposure to the driver and his copilot for the first application.

The chloropicrin results varied widely, ranging from below the limit of detection up to 181 ppb (see Table 1). Three of the 10 chloropicrin samples (driver: 2 of 5; copilot: 1 of 4; shoveler: 0 of 1) were above the PEL of 100 ppb. There does not appear to be a correlation between the levels of chloropicrin for the driver and his copilot or with the corresponding methyl bromide levels (see Graphs 1-4) [One chloropicrin sample for the copilot was voided (front sample tube was lost in the field) while the difference between chloropicrin values (80 ppb vs. ND) in the fourth sampling period (see Graphs 3 and 4) precluded establishing any exposure relationships.]

TWAs for methyl bromide and chloropicrin were calculated for workers whose exposure was measured two or more times per fumigation. These values are: (1) driver, day 1: (a) methyl bromide: 1.4 ppm, (b) chloropicrin: 69 ppb; (2) copilot, day 1: (a) methyl bromide: 1.6 ppm, (b) chloropicrin: 41 ppb. Total monitoring time (135 or 180 minutes) was used as basis of actual exposure in calculating the TWAs. TWA calculations for worker exposure on day 2 were not done because workers were monitored only once.

Analysis of the samples in which breakthrough occurred shows that it is not a serious problem. Only one of 11 methyl bromide samples showed more than 10 percent breakthrough into the back section of the charcoal tube. Breakthrough into the third section of the chloropicrin sampling train was negligible (all were down near the limit of detectability) and one of the 10 samples had greater than 10 percent in the second section of the first tube.

Downwind concentrations of methyl bromide and chloropicrin were also monitored. This data is discussed in a separate report (HS-1061).

CONCLUSIONS

The levels of methyl bromide measured for workers during preplant soil fumigations are well within the acceptable exposure limits and do not pose a health hazard to the workers. These results confirm the results from a prior methyl bromide study done in 1981 by the Worker Health and Safety Unit. On the other hand, the margin of safety may be very small for chloropicrin. However, due to severe irritation of the eyes and mucous membranes at low concentrations, the National Institute of Occupational Safety and Health considers it to be a material with good warning properties for the workplace environment. More field fumigation monitoring is needed to further characterize worker exposure and determine compliance with exposure standards for this type of work activity.

Table 1

Potential Inhalation of Methyl Bromide and Chloropicrin by Workers During Preplant Soil Fumigation in Orange County

Study Site #	Sampling Time (minutes)	Driver's Breathing Zone		Copilot's Breathing Zone		Shoveler's Breathing Zone		Air Temp. °F	Soil Temp. °F
		Methyl Bromide (ppm)	Chloropicrin (ppb)	Methyl Bromide (ppm)	Chloropicrin (ppb)	Methyl Bromide (ppm)	Chloropicrin (ppb)		
1	45	3.4	106	4.2	96	---	---	71	73
	45	0.8	47	0.6	26	---	---	74	73
	45	1.2	43	1.0	---(1)	---	---	74	73
	45	0.4	80	0.7	---(2)	---	---	82	73
2	45	2.5	126	6.3	181	0.7	45	67	73

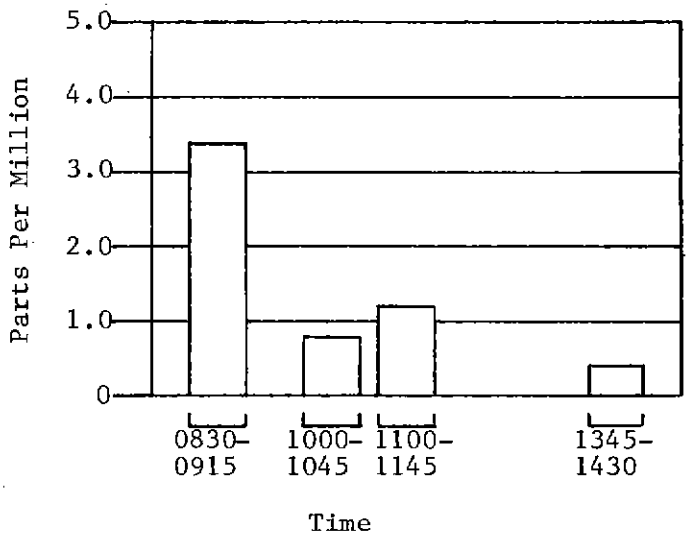
For study site # 1, Terr-o-gas 67 (EPA # 5785-24-AA) was applied at a rate of 300 lbs./A. At this rate 201 lbs. of methyl bromide and 95.4 lbs. of chloropicrin were applied per acre. For study site # 2, Tri-Con 75/25 (EPA # 11220-50007-AA) was applied at a rate of 275 lbs./A. At this rate 206¼ lbs. of methyl bromide and 68$^{3}/_{4}$ lbs. of chloropicrin were applied per acre.

(1) Invalid sample - front sample tube lost.

(2) MDL for chloropicrin is 1.0 ppb.

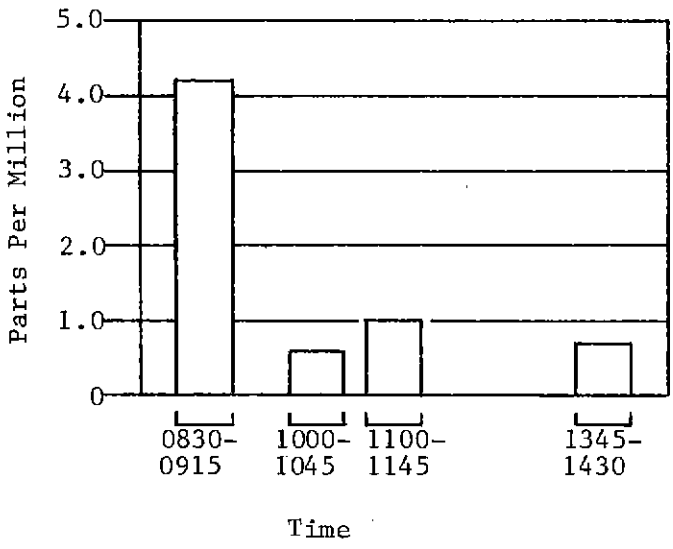
GRAPH 1

Measured Concentrations
of Methyl Bromide in the Breathing Zone
of the Driver During Preplant Soil
Fumigation #1



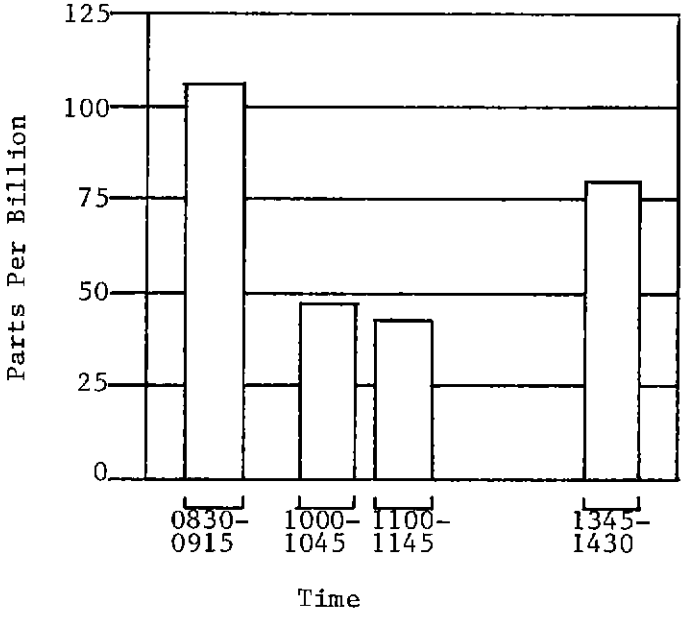
GRAPH 2

Measured Concentrations
of Methyl Bromide in the Breathing Zone
of the Copilot During Preplant Soil
Fumigation #1



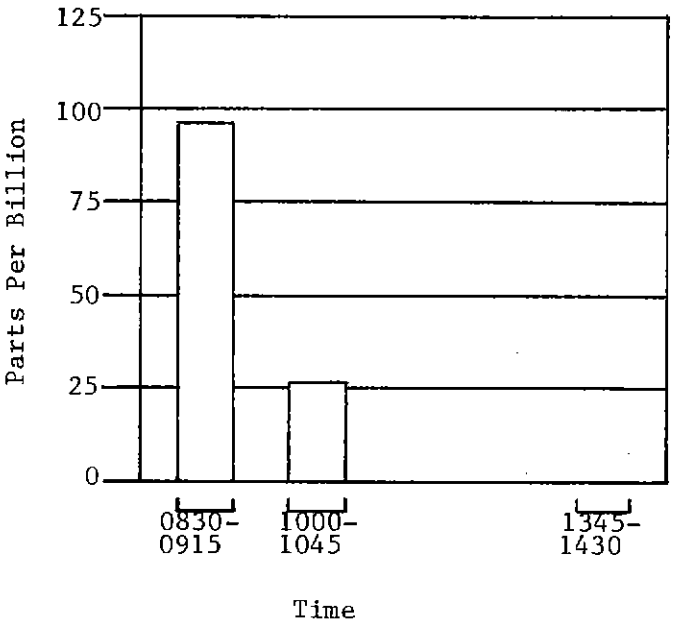
GRAPH 3

Measured Concentrations
of Chloropicrin in the Breathing Zone
of the Driver During Preplant Soil
Fumigation #1



GRAPH 4

Measured Concentrations
of Chloropicrin in the Breathing Zone
of the Copilot During Preplant Soil
Fumigation #1



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3. Amoore, J. E. and E. Hautala. Odor as an Aid to Chemical Safety. Odor Thresholds Compared with Threshold Limit Values and Volatilities for Industrial Chemicals (In Press).

4. National Institute for Occupational Safety and Health/Occupational Safety and Health Administration. 1981. Occupational Health Guidelines for Chloropicrin. Occupational Health Guidelines for Chemical Hazards. Washington, D.C.

DETERMINATION OF METHYL BROMIDE ON CHARCOAL TUBES

Scope

This method is for the desorption and analysis of methyl bromide from charcoal air sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

Principle

Methyl bromide (MeBr) that has been adsorbed from the air onto activated charcoal is desorbed from the charcoal with ethyl acetate, diluted as needed and analytically determined by gas chromatography using flame ionization or electron capture detection.

Reagents and Equipment

1. Ethyl acetate, nanograde.
2. Analytical grade methyl bromide.
3. Approved and calibrated personal sampling pump.
4. Charcoal tubes--SKC #226-09.
5. Developing vials with teflon liners--SKC #226-02.
6. Assorted microsyringes for preparing standards and gas chromatography.
7. Assorted pipets.
8. Volumetric flasks.
9. Small triangular file for scoring glass tubes.
10. Gas sampling bulb--Supelco 500 ml. with septum (#2-2148).

Analysis

Interferences: High humidity may affect trapping efficiency.

1. Score each charcoal tube with a file in front of the first section of charcoal.
2. Break open the tube. Remove and discard the glass wool.
3. Transfer the charcoal in the upstream section to a labeled desorption vial which contains a known amount of nanograde ethyl acetate. 2-4 ml. is suggested. Adding solvent to the charcoal may cause loss of MeBr.

4. Remove and discard the foam partition from the tube.

5. Transfer the second section of charcoal to a second labeled desorption vial which contains a known amount of nanograde ethyl acetate.

6. Allow the samples to desorb for one hour while rotating @30 rpm.

7. Transfer an aliquot to a sample storage vial, label, and freeze until analysis time.

8. Determine by GLC.

Determination of Desorption Efficiency

1. Inject a known amount of MeBr (1 microgram to several milligrams) into the charcoal with a syringe and cap the tube with the supplied caps. The tube should be from the same lot that was used for the samples.

2. At least five tubes (preferably at levels covering the expected range) should be prepared in this manner and allowed to stand at least overnight to assure complete adsorption. A blank tube should be treated the same way except that no sample is added.

3. Analyze the tubes by the analytical procedure.

4. Desorption efficiency = $\frac{\text{Response sample-response blank}}{\text{Response standard}}$

   The standard(s) should be the same amount as injected into the charcoal tubes. This eliminates standard variation errors.

Calculations:

1. Determine weight of MeBr present on charcoal tube sections by GLC analysis.

2. Correct this total weight of MeBr by subtracting any blank value present on the blank tube.

3. The corrected weight is divided by the desorption efficiency to obtain the final weight of MeBr present.

4. The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$VS = \frac{V \times P \times 298}{760 \times (T+273)}$$

Where VS = Volume of air at standard conditions.
V = Volume of air as measured.
P = Barometric pressure in mm Hg.
T = Temperature of air in °C.

5. Calculate ppb in air from the above data.

$$\text{ppb (volume basis)} = \frac{\text{ng} \times 24.45}{\text{VS} \times 94.9} = \frac{\text{ng}}{\text{VS}} \times 0.2576$$

24.45 is the mole volume of MeBr at 25° and 760 mm.
94.9 is the molecular weight of MeBr.

Gas Chromatographic Conditions:

Gas chromatograph with Ni^{63}, H^3, or flame ionization detector.

Temperatures - Injector: 125°C
Detector: Follow manufacturer's suggestions

Column: 20' x 1/8" O.D. nickel tubing
10% SP-2100 on 100/120 Chromosorb W-HP
70°C, 10 ml/min N_2 carrier gas
MeBr retention time approximately 1.9 minutes

Column: 6' x 2 mm I.D. glass
80/100 Poropak Q
130°C, 30 ml/min N_2 carrier gas
MeBr retention time approximately 1.4 minutes

Column: 20' x 1/8" O.D. nickel tubing
10% FFAP on 100/120 Chromosorb W-HP
70°C, 25 ml/min N_2 carrier gas
MeBr retention time approximately 1.9 minutes

References

1. NIOSH Manual of Analytical Methods, Second Edition. Method S372. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402.

2. Determination of EDB on Charcoal Tubes, California Department of Food and Agriculture, Chemistry Laboratory Services, 3292 Meadowview Road, Sacramento, California 94832.

3. Malone, B., Analysis of Grains for Multiple Residues of Organic Fumigants. AOAC, 52, p. 800, 1969.

4. Clower, M., Modification of the AOAC Method for Fumigants in Wheat. FDA Laboratory Information Bulletin #2169, August 1978.

5. Mr. Mario Fraccia, Air Industrial Hygiene Lab, Berkeley, California. Personal Communication.

THE ANALYSIS OF AIR SAMPLES FOR CHLOROPICRIN

SCOPE:

This analysis is for the determination of chloropicrin on XAD-4 resin air sample tubes.

PRINCIPLE:

Chloropicrin is trapped on XAD-4 tubes at the sampling site, frozen during transport to the lab, desorbed with ethyl acetate, and analyzed on a capillary GLC using electron capture detection.

REAGENTS AND EQUIPMENT:

1. ethyl acetate--pesticide grade, checked for interferences
2. Appropriate glassware
3. Gas Chromatograph

Instrument:	Hewlett Packard 5880 with ECD detector at 300° C.
Column:	30 M x .25 mm J&W 1701 at 40 C. Operated in split mode--approx. 100:1 split
	Column pressure: 20 psi
	Split flow: 40 ml/min
Injector:	Split injector liner at 220 C.

Under these conditions chloropicrin elutes in 6.5 minutes.

ANALYSIS:

Break the XAD-4 tubes and place the resin in 5 ml vials containing 4 ml ethyl acetate. Desorb tubes for an hour on a rotator. Proceed to the GLC with no further preparation.

DESORPTION COEFFICIENT:

The desorption coefficient is 94% at the 2 microgram/spl level.

CALCULATIONS:

Results should be reported in ppb and mg/m^3 using the appropriate air sample calculations. The molecular weight of chloropicrin is 164.4.

DISCUSSION:

At the present time, a single sample consists of two tubes in series. The entire first tube is treated as the 'front'

section, and the second tube is treated as two additional sections. This system was used to check out breakthrough. If the sample size is kept to 10 L or less, and the sample flow rate is about 200 ml/min, the breakthrough will be 10% or less.

Recoveries are 94% for levels of about 30 ppb, or 2 UG/spl.

REFERENCES:

Guide to Chemicals Used in Crop Production, Information Canada, p. 118, 1973.

NIOSH Manual of Analytical Methods, Method S212, S104, 260.